Experimental report

"Studies of hydrogen induced phase-structural transformations in $LaNi_5$-related materials"

Principal investigators:

Volodymyr A. Yartys, Jan Petter Mæhlen, and Marit S.S. Stange, IFE, Norway

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Summary

Hydrogen storage materials are characterized by amazingly fast rates of H exchange with H_2 gas. *In situ* Synchrotron X-ray Powder Diffraction (SR-XRD) is a very valuable tool in probing mechanism of H uptake and release and allows to study kinetics, mechanism of the transformations and structure of the metal and hydrogen sublattices. This work was aimed on studies of the hydrogenation and dehydrogenation processes in a selected Sn-modified AB5 metal hydride systems ($LaNi_{4.7}Sn_{0.3}$-H_x) by *in situ* SR-XRD at H_2 pressures 0 - 6 bar and temperatures from 200 to 375 K. A specially designed cell for *in situ* studies in H_2-atmosphere was utilised. The cell is attached to a metal hydride hydrogen storage unit developed at IFE providing hydrogen gas at convenient pressures. The work benefits form a possibility to control hydrogen content in the nonstable at ambient conditions materials by settling increased H_2 pressures and/or decreased temperatures.
In the current experiments, main focus was on hydrogen uptake and release at low temperatures. A phase transformation with indications of formation of an intermediate phase was observed.

Experimental setup

A setup designed for *in situ* studies of the chemical processes in hydrogen gas/vacuum [1-3] was used. A small amount of the sample is contained in a quartz glass capillary (with inner diameter of 0.3, 0.5 or 0.7 mm) and fills approximately 1–2 mm in its bottom part. The capillary is hermetically connected to the gaseous system using a carbon ferrule mounted in a T-piece, which, in turn, is attached to the goniometer head. A two-stringed flow system makes it possible to switch between hydrogen gas and vacuum during the experiment. The fixed connection of the microreaction cell to the goniometer head makes a full rotation of the sample difficult. However, the averaging over the different orientations of the crystallites, resulting in the elimination of the preferred orientation effects in the collected diffraction data is achieved by applying wobbling of the setup around the axis of the capillary using a flexible PEEK (Polyetheretherketon) tubing connection between the microreaction cell and the flow system. During the experiments, hydrogen gas is supplied from a portable metal hydride storage unit developed at IFE, Kjeller ($La_{1-x}Mm_xNi_5$ hydrogen storage alloy). Vacuum is created using a turbo molecular vacuum pump. Except for the PEEK tubing allowing the wobbling of the sample cell, stainless steel tubes are used for the connections to prevent oxygen diffusion through the tubes during the experiments.

Experiments at the BM01A station were collected using a MAR image plate detector. Wavelength and sample-to-detector distance were calibrated from individual runs of LaB_6. Typical, a time resolution of ~2 minute was used (20-60 seconds for data collection and about 85 seconds for processing/reading of the image plate) with 2θ range of about 1-30°. To obtain data suitable for whole-profile refinements, the 2D patterns were integrated to 1D using the Fit2D program [4].

Results

Activation of the $LaNi_{4.7}Sn_{0.3}$ sample was performed by heating in H_2 at 100°C for about 10 minutes. The first hydrogenation attempts were performed in steps of 20 K from 320 down to 200 K in 6 bar H_2 pressures. Small traces of β hydride was observed (5-7 wt.%) at all temperatures. Volumes of the unit cells as a function of temperature is shown in the figure below (Figure 1). Then the temperature was gradually increased again and the sample was put under dynamic vacuum. At 340K, introducing ~6 bar of hydrogen in the system, a very fast hydrogenation process was observed (Figure 2). During the fast transformation, an indication of formation of a secondary intermediate phase was observed.

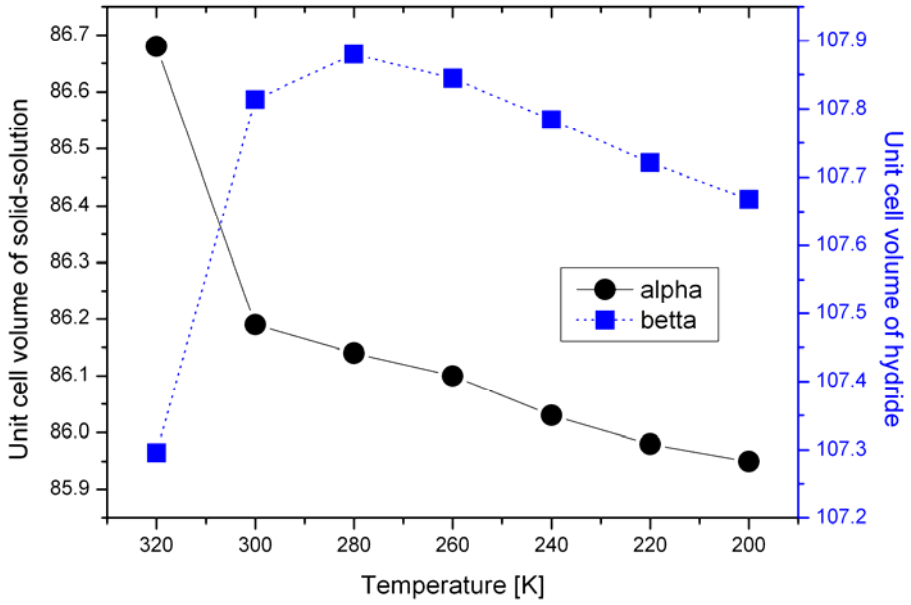

Figure 1: Evolution of hydride and alloy (solid-solution) unit cell volumes as a function of temperature @ 6 bar H_2.

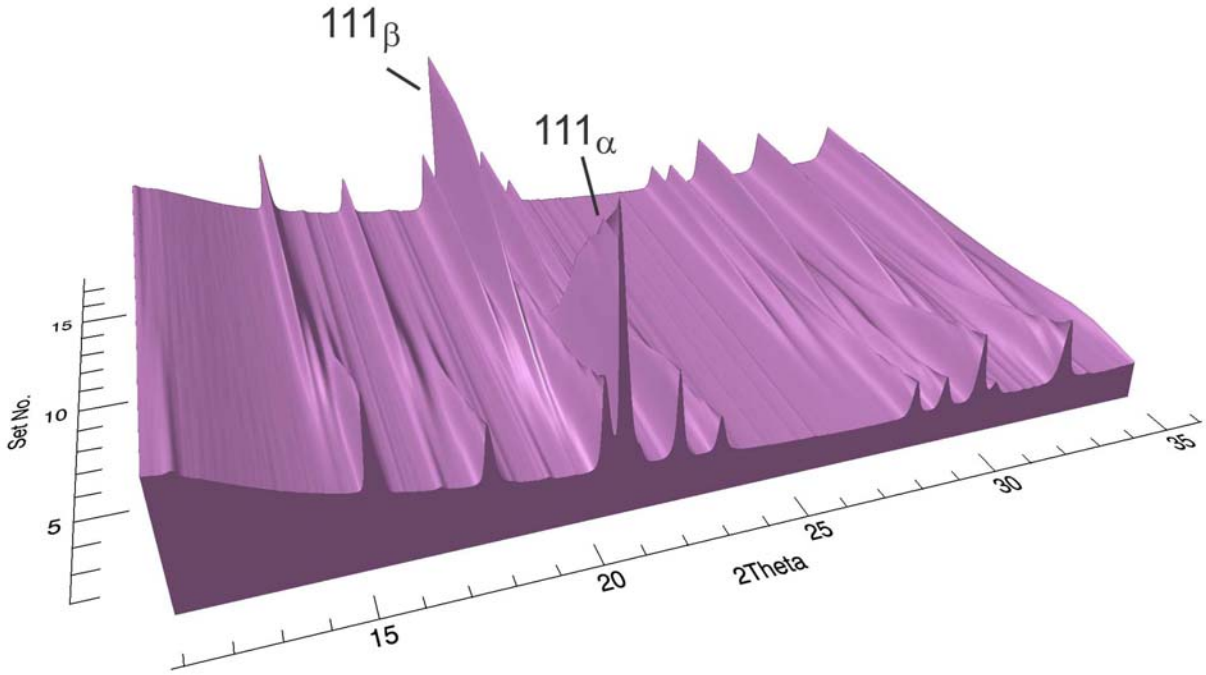

Figure 2: SR-XRD histograms (λ = 0.8 Å) during hydrogen uptake by $LaNi_{4.7}Sn_{0.3}$ at 340K and 6 bar H_2. A fast transformation from solid-solution (α) to hydride phase (β) is observed.

Following that, absorption / desorption runs were performed at different temperatures (340 K, 300-375 K, 360 K, 200-360 K). Very fast phase transformation was observed at higher temperatures (375 K), however, due to technical problems, time did not allow installing measuring system needed for measuring these fast reactions.

The experiments gave valuable insight into the α-β phase transformation in the technically very important Sn substituted $LaNi_{4.7}Sn_{0.3}$-H system.

References

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4 Fit2D (http://www.esrf.eu/computing/scientific/FIT2D/)